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Energy Transfer at High Temperatures in the

Cyclopropane VEM System.   Temperature Dependence of $<\Delta E'>$.

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The study of collisional energy transfer between cyclopropane molecules and a seasoned silica wall by the Variable Encounter Method has been extended upward in temperature to 1325 K. The value of <ΔE'> the average energy of a down-transition upon collision of the substrate with the wall continues to decrease monotonically. The data provide the most accurate and well-documented display of the temperature trend of <ΔE'> presently available.

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Energy Transfer at High Temperatures in the Cyclopropane VEM System.

Temperature Dependence of $\langle\Delta E\rangle$.[1]

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Abstract

The study of collisional energy transfer between cyclopropane molecules and a seasoned silica wall by the Variable Encounter Method has been extended upward in temperature to 1325 K. The value of $\langle\Delta E'\rangle$ the average energy of a down-transition upon collision of the substrate with the wall continues to decrease monotonically. The data provide the most accurate and well-documented display of the temperature trend of $\langle\Delta E'\rangle$ presently available.

Recently, collisional energy transfer data have been obtained in steady-state homogeneous thermal unimolecular polyatomic systems at temperatures of 773 K[2a], 973 K[2a] and 1173 K[2b], with cyclopropane-d_2 and cyclopropane substrates. These studies were made with various monatomic, diatomic and polyatomic bath gases and indicate that the relative collision efficiency, β_c , and the average amount of energy transferred on a <u>downstep</u> transition, $<\Delta E'>$, both decrease with increase of temperature. Very weak colliders such as helium have been predicted on theoretical grounds[3] to follow a power law, $\beta_c \propto T^{-n}$, where $n > 2$. Some anomalies in shock tube work at temperatures around 1200 K - 1500 K have previously led to the suggestion that the trend in β_c may extend to significantly higher temperatures.[4,5] By contrast, a recent shock tube study[6] has led to the suggestion that $<\Delta E'>$ increases with rise of temperature for helium bath gas, although contradictory data exists.[2]

A decline of $<\Delta E'>$ with rise of temperature has also been observed in studies made by the recently developed Variable Encounter Method (VEM) for a variety of hydrocarbon substrate molecules,[7-10] over the range from above 400 K to above 1100 K. The collision partner in these studies was the seasoned wall surface, assumed to behave like a large polymeric molecule of effectively infinite mass. It is important to extend these approaches well into the high temperature region in order to link more firmly the results at lower temperatures with the shock tube regime. In the work reported here, we have extended the VEM study of the collisional relaxation of vibrational transients in the cyclopropane system up to 1325 K.

The details of the practise and theory of the experimental method are similar to previous studies.[7-10] Average numbers of collisions of substrate molecules per encounter with the reactor surface, m, were 5.6 and 7.6 in the present work. The purity of the reactant cyclopropane was 99.94%. Analysis of the reaction products was by gas chromatography with a squalane column and f.i.d.

Figure 1 shows experimental plots of the average reaction probability per collision, $\bar{P}_c(m)$ versus temperature from 1020 K to 1325 K. The data were compared with stochastic calculations using several models for the energy transfer transition probabilities, $P_{\Delta E}$; details are provided in ref. 7. The threshold energy E_0 was taken as 63.6 kcal mol^{-1}. The best fit to the data is obtained with a gaussian model: $P_{\Delta E} = A \exp\{-(\Delta E - \Delta E_{mp})^2 / 2\sigma^2\}$; where A is a normalization constant; ΔE_{mp} is the most probable downstep energy trans-ferred (independent of initial energy), and σ was set equal to 0.7 ΔE_{mp}. Calcu-lated curves were fitted to the data (Fig. 1). Values of $<\Delta E'>$ (cm^{-1}) that fit the data from both reactors at particular temperatures are shown, and the trend of decreasing $<\Delta E'>$ with increasing temperature is seen to continue throughout the temperature range studied. As shown in Fig. 2, these values are almost identical to, but a little less ($\sim$ 30 cm^{-1}) than those reported for cyclopropane by Flowers et al.[9] in the region of temperature overlap.

As was mentioned elsewhere,[10] the most reliable data tend to be obtained at higher temperatures, where complexities due to surface catalytic effects are minimized. Paradoxically, the work in ref. 9 showed a slight and increasing catalytic side reaction of acetylene production, at and above 1000 K. Careful chemical analysis in the present study revealed no acetylene side reaction. Since both studies give rise to almost identical wall activation efficiencies, the assertion of Flowers, et al. that acetylene production represented a minor, and irrelevant side reaction is borne out.

Incubation times[7] τ_{inc} have been defined previously and have been related to the mean first passage time, $\bar{t}_{fp}$, by the expression[7]

$$\tau_{inc} = \bar{t}_{fp} - t_{fp}^{ss}$$

where $\bar{t}_{fp}^{ss}$ is the steady state mean first passage time and $\bar{t}_{fp}$ is the mean first passage time for the case of transients,

$$\bar{t}_{fp} = \int_0^\infty t\, P(t)\, dt \; ,$$

where $P(t)$ is the probability that a molecule will cross the reaction thres-hold E_0, for the first time, at time t. $\bar{\tau}_{inc}$ also increases with temperature in this study as $<\Delta E'>$ declines, from 13.5 collisions at $\sim$ 1040 K to 18.6 collisions at 1300 K. Incubation times greater than unity signify, of course, that the conventional relative collisional efficiency, β_c , is less than unity, i.e., less than strong collider values.

In conclusion, the data of Figure 2 provide the most accurate illustra-tion presently available of an example of a trend of $<\Delta E'>$ over a wide range of temperatures.

The decrease in $<\Delta E'>$ and β_c with rise of temperature can be explained as follows. A semi-empirical quasi-statistical accommodation model for colli-sional energy transfer, subject to conservation of angular momentum restrictions, was described some time ago by Lin and Rabinovitch.[3] Oref and Rabinovitch[15] gave a theoretical treatment based on this model. In etiher version, a decrease in $<\Delta E>$ with increase in temperature is predicted. The treatment of Lin and Rabinovitch took the form for the average of a down-transition, $<\Delta E'>$,

$$<\Delta E'> = \frac{\displaystyle\sum_{\Delta E = E_{th}}^{E_{tot}-E_0'} P(\Delta E) B(E_{th})[\Delta E - E_{th}]}{\sum P(\Delta E)\, B(E_{th})} \; ;$$

where, E_{th} is the thermal energy of transitional modes (3 to 6, depending on the nature of the collision partner) that are formed in the collision complex; E_{tot} is the total internal energy of the substrate molecule and the transitional modes; E_0' is the dissociation energy of the collision complex; $P(\Delta E)$ is the probability of, and ΔE is the energy in the transitional modes at the time of decomposition of the complex. The negative temperature behavior arises because

E_{th} increases more strongly with T than does either the total energy of the collision complex or ΔE. In addition, decrease of the residence time of molecules on the surface with increase of temperature further weakens the practical realization of the limiting assertion of quasi-statistical energy relaxation.

We may expect for weak colliders, especially He, that at sufficiently high temperatures, the collision-complex accommodation model[3] may give way to the Landau-Teller-type behavior for polyatomic molecules, as has been found previously (starting at much lower temperatures) for diatomics,[11] and as appears may be likely[6] for triatomics near, or above 2000 K. Whether such alteration of behavior will be seen at practical temperatures for the case of interaction of polyatomic substrates with fairly strong colliders is more problematical.
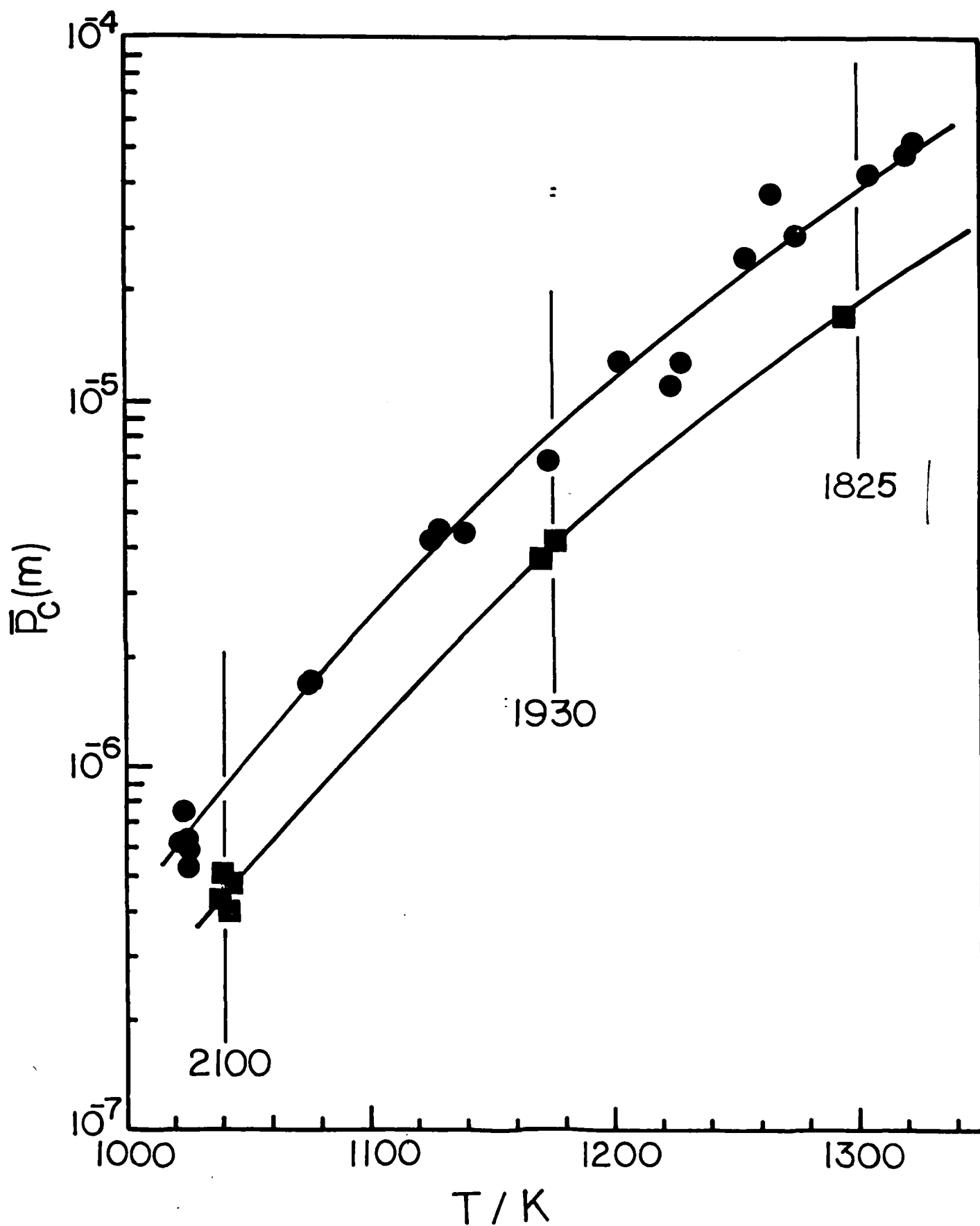
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Figure Captions

Figure 1   Plots of experimental values of $\bar{P}_c(m)$ <u>vs</u> temperature for the
           two reactors: m = 7.6, ● ;   m ≈ 5.6, ■ . Also shown are
           solid curves calculated using a gaussian transition probability
           model fitted to the m = 5.6 data at each of three values of T.
           The <ΔE'> values (cm^{-1}) were then used to construct the calculated
           curve for m = 7.6.

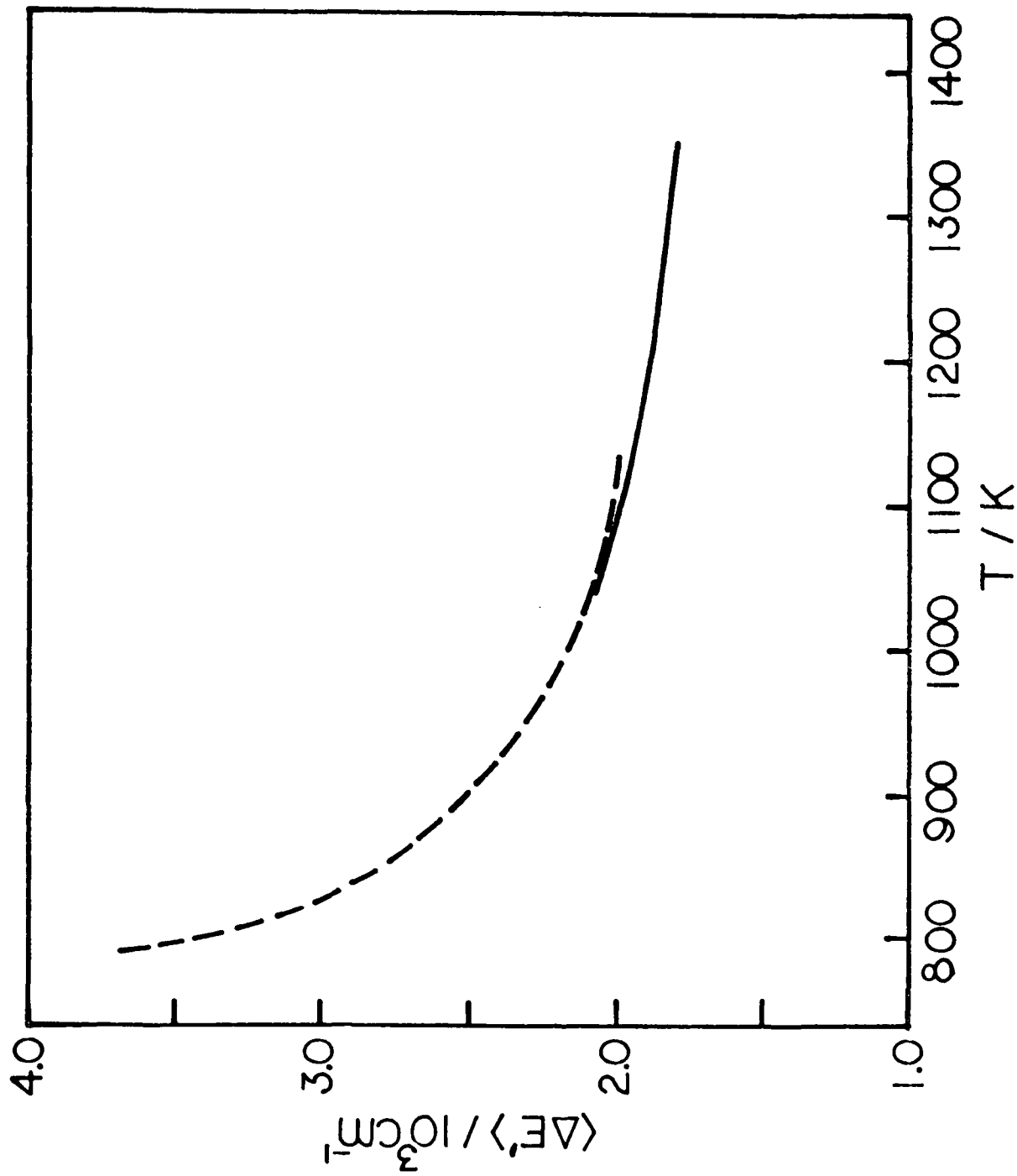Figure 2   Calculated plots of <ΔE'> versus temperature for cyclopropane:
           data of Flowers et al. (ref. 9), - - - ; present data, ── .

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